

PATENT SPECIFICATION

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(54) PROCESS FOR PREPARING CHLORINATED HYDROCARBONS

(71) We, THE DOW CHEMICAL COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of Midland, County of Midland, State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to the preparation of chlorinated hydrocarbons.

In the preparation of chlorinated hydrocarbons by the oxychlorination reaction, e.g., employing ethylene, oxygen and hydrogen chloride in the vapor phase at an elevated temperature over a Deacon-type catalyst to produce 1,2-dichloroethane (ethylene dichloride), it is common practice to employ air as the source of oxygen. It is also common practice to employ an excess of both oxygen, as air, and hydrogen chloride over that amount which would be stoichiometrically required to react with the ethylene in the feed. In order to obtain the maximum throughput of reactants in a given reactor, super-atmospheric pressure is usually employed. Both the excess of oxygen (as air) and high pressure are unavoidably detrimental when using air as the source of oxygen, since the nitrogen of the air employed must be compressed and circulated along with the oxygen. This requires large compressors and containers and also makes it difficult and expensive to remove products or pollutants from a vent stream containing such large volumes of inerts.

As larger production facilities are built, it becomes highly desirable to have a process in which the vented gases are reduced to abate pollution, and to recover the greatly increased volume of valuable products normally found in vent or off-gases.

The present invention comprises a process for preparing chlorinated hydrocarbons which comprises contacting a mixture of oxygen or

a gas containing molecular oxygen, hydrogen chloride and an ethylenically unsaturated aliphatic hydrocarbon or a partially chlorinated ethylenically unsaturated aliphatic hydrocarbon, the oxygen being employed in a state of purity of not less than 50% with respect to noncondensable gases, in amounts of from 0.4 to 0.8 mole of oxygen and 1.8 to 2.2 moles of hydrogen chloride per mole of said unsaturated hydrocarbon, with a Deacon-type copper oxychlorination catalyst at a temperature and pressure at which oxychlorination occurs, treating the resulting oxychlorination reaction products with water to remove any unreacted hydrogen chloride, cooling the remainder of the products to remove the condensable chlorinated hydrocarbons and recycling sufficient remaining noncondensable gases to the reactor to supply from 30 to 60 percent of the feed.

Preferably, the reaction is carried out in a plurality of tubular reactors which are externally cooled to maintain the temperature therein at from 180° to 350°C.

Preferably the state of purity of the oxygen is greater than 90% and more preferably substantially pure oxygen is employed. The state of purity with respect to condensable inerts such as water vapor is likewise greater than 50%. The condensable inerts are critical only with respect to equipment size for a given output and temperature profile throughout the reactor. If desired, the oxygen may be in admixture with steam. The noncondensable products of reaction, excluding the unreacted HCl, in excess of those required for recycle to maintain the system under the desired pressure and volume, are removed from the system. The noncondensable products consist of the oxidation by-products, the HCl by-products and minor impurities introduced in the feed reactants and are the sole gases utilized as recycle. The portion of these noncondensables not recycled constitute the off-gas from the system. The off-gases from the sys-

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tem consist of a maximum of 1—2 lbs. (0.45—0.90 kg.) of noncondensibles per 100 lbs. (45.4 kg.) of desired product. The off-gas, when the oxygen is essentially pure with respect to noncondensibles such as nitrogen, is in a more suitable state for nonpolluting disposal than the off-gases normally associated with oxychlorination processes in use today. For example, the off-gas of the present invention, using an oxygen of greater than 50% with respect to noncondensibles has a fuel value sufficient to sustain burning. In addition, the useful by-products carried out of the reactor in the off-gas are present in an amount in the off-gas sufficient to make recovery practical. Recovery of the unreacted ethylene from the off-gas becomes practicable when the oxygen introduced into the reactor contains less than 50% non-condensable inerts, and preferably less than 10%. It is, of course, to be understood that if the oxygen contains more than 50% non-condensable inert gas, then the fuel value is decreased and it becomes impracticable to recover the usable by-products.

In accordance with the present invention, a major reduction in undesirable effluent gases is achieved accompanied by improved selectivities (yield), conversions, productivities, temperature control, stability of operation and flexibility of production.

Good results have been obtained by the introduction of ethylene, as the hydrocarbon reactant along with recycle gases, preferably preheated, before or after mixing, to between 100° to 200°C. A mixture of oxygen and hydrogen chloride, preferably preheated to a temperature of from 50° to 200°C. is also introduced into the system. The oxygen and hydrogen chloride preferably are essentially pure prior to mixing. After mixing and preheating, the two streams are mixed together under conditions to preclude explosive mixtures being formed, the oxygen concentration being less than 15 percent oxygen based on total mixture volume. The resulting mixture which consists of 1.8 to 2.2 moles HCl, 0.4 to 0.8 mole O₂, per mole of unsaturated aliphatic hydrocarbon and 30 to 60 mole percent, based on the total mixture of recycle noncondensable gases is introduced to a tubular reactor containing a Deacon catalyst, maintained at a temperature of from 190° to 300°C. and under a pressure of from 15 to 100 psig (1.05—7.0 kg./cm.²). The flow rate is in the range of 50—1150 lbs. (22.5—517 kg.) HCl per cubic ft. (28.3 liters) of reactor volume per day.

The effluent from the reactor is contacted with hot water (e.g., 50°C. or higher) to dissolve the unreacted hydrogen chloride, and the resulting gas mixture is passed to a condenser where the product water and condensable chlorinated hydrocarbons are condensed and withdrawn. The remaining gas (noncondensibles) is then compressed to

reactor inlet pressure and sufficient of this gas is recycled to the reactor to supply 30 to 60 percent of the feed and the remainder is withdrawn.

The Deacon-type copper catalyst is any one of those known in the prior art including those catalysts which are promoted, as with potassium. Preferably the catalyst is copper as copper chloride loaded on alumina. The copper content of the load as percent weight of copper chloride and load is preferably from 1 to 10 percent, more preferably from 2% to 7%, and most preferably from 3% to 6.5%. The catalyst loaded alumina should be present in lower concentrations at the inlet than at the outlet. Thus, for example, the reactor preferably is divided into several zones of increasing copper content from inlet to outlet. This condition can be achieved by increasing the load of copper as copper chloride in the carrier from zone to zone or maintaining a constant copper as copper chloride load equal to the greatest percent copper desired and diluting the catalyst (copper as copper chloride on alumina) by admixture of the loaded carrier with inert or unloaded alumina or silica. Similar means of obtaining various concentrations of promoters is preferably also utilized.

The reactor can be substantially any metallic container capable of withstanding the temperatures and pressures of the reaction. The preferred and commonly employed reactors are tubular having internal diameters of from 0.5 to 3 inches (1.27—7.62 cm.), more preferably from 0.75 to 2 inches (1.90—5.10 cm.). The reactors can be of any suitable length but preferably range from 10 to 60 feet (3.05—18.3 meters). One or a plurality of reactors can be employed. When a plurality of reactors are employed they are formed into bundles with a common header for inlet and outlet. The tubes, whether single or bundles are surrounded by cooling medium such as oil, diphenyl ether-biphenyl eutectic mixture known as Dowtherm A (registered Trade Mark), the similar eutectic and isomeric mixture of higher boiling chlorinated aromatic ethers and chlorinated polyaromatic compounds.

In accordance with the present invention, useful unsaturated compounds which may be oxychlorinated are those containing two and three carbon atoms, for example, ethylene and propylene and their partially chlorinated derivatives, for example, vinyl chloride, vinylidene chloride, trichloro-ethylene, 1- and 2-chloropropenes, 1,1-dichloro-2-propene, 1,2-dichloro-2-propene, 1,3-dichloropropene, 1,1,2-trichloro-1-propene, and 1,2,3-trichloropropene.

In a representative operation in accordance with the foregoing procedure, the following results were obtained.

Example.			gas are mixed in a ratio of 0.51/1.96 lb.-mole (0.23—0.88 kg. mole) feed ratio and preheated to 80°C. and delivered to a five unit static mixer. Both streams are brought together and passed through a five unit static mixer, then into a bed of alumina contained in a 2" diameter by 1 foot long (5.1 × 30.5 cm.) tube. The gases exit the tube at about 100°C. and are passed immediately into a 1.5 inches diameter by 60 foot long (3.8 cm. × 18.3 meters) tubular reactor filled with 6—8 mm. spherical porous activated alumina catalyst support upon which copper as copper chloride has been deposited. The catalyst bed is divided into zones of increasing concentration by successively increasing, from inlet to outlet, the amount of loaded alumina support mixed with the diluent (unloaded support) and/or increasing the amount of catalytic material (copper as copper chloride) on the support as, for example, in the following scheme:	
Ethylene and a recycle stream consisting of:				
		Mole Percent		
5	O ₂	1.93		20
	CO	39.3		
	CO ₂	38.4		25
	CH ₄	6.07		
	C ₂ H ₄	9.13		
10	C ₂ H ₆	0.6		
	N ₂	2.15		30
	1,2-C ₂ H ₄ Cl ₂	1.66		
	C ₂ H ₅ Cl	0.781		
	C ₂ H ₃ Cl	0.048		
15	are mixed in the ratio of 1/2.04 lb.-mole (0.45—0.92 kg.-mole) feed ratio, preheated to about 140°C. and delivered to a five unit static mixer. Oxygen and hydrogen chloride			35

Distance from Inlet in Feet (Meters)			Wt. % Copper * Vol. % Loaded
0.0—0.5	(0.15)	(inlet)	0/100
0.5—15	(0.15—4.58)		3.6/14
15—25	(4.58—7.63)		3.6/30
25—35	(7.63—10.68)		3.6/50
35—45	(10.68—13.73)		3.6/100
45—60	(13.73—18.3)	(outlet)	6.0/100

* Wt. copper is calculated as that of elementary copper, not copper chloride, although it is on the loaded alumina as copper chloride.

- 40 The gaseous effluent exiting the reactor is cooled in a 1.5" × 4 ft. (3.8 cm. × 1.22 meters) packed, glass-lined water-cooled condenser, and is then counter-currently contacted with water in a packed 6" × 10' tower (15.2 cm. × 3.05 meters). The unreacted hydrogen chloride is dissolved in the water and the major portion of the chlorinated product is condensed in this tower. The non-condensable gases are taken off the top of the tower and recompressed to reactor pressure. The liquids are delivered to a flash drum under 1 psig. (0.07 kg./cm²) and dissolved gases flashed
- off. These gases are delivered to a dryer and then recompressed and combined with the gases from the tower. The liquids remaining in the flash drum are sent to a phase separator wherein the organic liquids are separated from the aqueous phase. The organic phase is distilled to recover the ethylene dichloride. Those chlorinated hydrocarbons boiling below ethylene dichloride may be compressed and recycled. Those boiling higher than ethylene dichloride are removed and may be cracked to usable unsaturates.

Feed Ratio of Reactants	Lb.—Moles./Day./Tube	(Kg.—moles)
C ₂ H ₄	6.29	(2.82)
HCl	12.33	(5.54)
O ₂	3.71	(1.66)
Recycle Gas	12.83	(5.80)
Vent Rate to Atmosphere *	0.288	(1.30)
<u>Operating Data</u>		
Inlet Pressure, psig. (kg./cm. ²)	90	(6.32)
Outlet Pressure, psig. (kg./cm. ²)	60	(4.22)
Recovery System Pressure, psig. (kg./cm. ²)	55	(3.87)
High Temperature in Reactor, °C.	275	
Low Temperature in Reactor, °C	222	
C ₂ H ₄ Conversion, %	99.6	
HCl Conversion, %	99.1	
C ₂ H ₄ Loss to Oxidation, %	2.58	
C ₂ H ₄ Yield to EDC, %	94.8	
HCl Yield to EDC, %	96.8	
Productivity, Lbs. EDC/ft. ³ /day **	1098	(497 kg./28.3 liters/day)

* The vent gas composition and the recycle gas composition are the same and were based on an average m.w. of 37.

**Productivity is defined as pounds of 1,2-dichloroethane produced per cubic foot of reactor volume per day.

Recycle Gas Composition Or Vent Gas Composition	Mole Percent	Condensed Product Phase Analysis	Weight Percent	15
O ₂	1.93	C ₂ H ₃ Cl	0.038	
CO	39.3	C ₂ H ₅ Cl	1.11	
CO ₂	38.4	CCl ₄	0	
CH ₄	6.07	Trans—C ₂ H ₂ Cl ₂	0.052	20
C ₂ H ₄	9.13	Cis—C ₂ H ₂ Cl ₂	0.093	
C ₂ H ₆	0.6	C ₂ Cl ₄	0	
N ₂	2.15	Sym—C ₂ H ₂ Cl ₄	0.029	
C ₂ H ₃ Cl ₂ (EDC)	1.66	Unsym—C ₂ H ₂ Cl ₄	0	
C ₂ H ₅ Cl	0.781	Beta—C ₂ H ₃ Cl ₃	0.59	25
C ₂ H ₃ Cl	0.048	C ₂ HCl ₃	0	
		C ₂ HOCl ₃	0.19	
		C ₂ H ₄ Cl ₂ (EDC)	97.89	
	100.069		99.992	

Scrubber Water Analysis	Weight Percent
$C_2H_5Cl_2$	0.84
C_2HOCl_3	0.196

5 In another representative operation of the process the flexibility of operation of the present invention was compared to that of a similar system which employed compressed air as its source of oxygen and which provided no recycling of reactor effluent. The present process was operated at 10% of its reactant capacity throughput. The recycled effluent rate was maintained at 30% of its capacity throughput as given in the previous example. Maximum reactor temperatures of 250—260°C. were observed, and % ethylene/hydrogen chloride conversions of 98—99/92—94 were achieved.

20 The above run was compared to the best existing commercial process, represented by a system using air as the source of oxygen and similar to that described in the present

process, except that it was comprised of a reactor consisting of 19 tubes instead of one. The comparison system was also scaled up accordingly in its condensing and scrubbing capacity. Upon repeated attempts to operate the process at 10% of throughput, the catalyst zone underwent large temperature rises surpassing 350°C. before being shut down. The coolant temperature was reduced from 225°C. to 205°C. and the reactor pressure reduced from 65 psig. to 25 psig. (4.55—1.76 kg.cm.²), with no improvement. Upon subsequent restoration of capacity reactant flows, the catalyst performance was found to be significantly impaired, resulting in reduced yields and hot spotting problems.

The above results may be directly compared to a commercial scale oxychlorination process which utilizes air as the source of the oxygen and vents all off-gases to a flare. In addition, two prior art processes are reported based on the data obtained from this patent specification. To obtain a meaningful comparison, the results are set side by side.

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Feed Ratio of Reactants

	Present Process		Existing Commercial Process		Prior Art			
					Penner ¹		Suzuki ²	
	Lbs. (kg.)/ Tube/Day	Mole Ratio	Lbs. (kg.)/ Tube/Day	Mole Ratio	Lbs. (kg.)/ Tube/Day	Mole Ratio	Lbs. (kg.)/ Tube/Day	Mole Ratio
C ₂ H ₄	176 (80)	1.0	114 (53)	1.0	26.4 (11.9)	1.0	6.0 (2.7)	1.0
HCl	450 (204)	1.96	290 (131)	1.97	72.4 (32.8)	2.11	16.3 (7.4)	1.96
O ₂	119 (54)	0.59	O ₂ /Air 81/351 (37/159)	0.64	15.6/67.4 (7.1/30.5)	0.52	3.0/16.7 (1.76/7.4)	0.53
Recycle Gas	359 (162)	2.04		0	0		11.8 (5.35)	

	Prior Art			
	Present Process	Existing Commercial Process	Penner ¹	Suzuki ²
Vent Rate* to Atm., Lb./100 lbs. EDC (Kg./100 Kg. EDC)	1.7	63.7	96.6	71.1
Inlet Pressure, psig. (Kg/cm. ²)	90 (6.32)	82 (5.8)	75 (5.3)	46 (3.2)
Outlet Pressure, psig., (Kg./cm. ²)	60 (4.22)	58 (4.1)	67 (4.7)	26 (1.8)
Recovery System Pressure, psig. (Kg./cm. ²)	55 (3.87)	44 (3.1)	—	—
High Temp. in Reactor, °C	275	277	296	340
Low Temp. in Reactor, °C.	222	219	232	315
C ₂ H ₄ Conversion, %	99.6	98.4	97.7	96.5
HCl Conversion, %	99.1	98.3	92.9	95.0
C ₂ H ₄ Loss to Oxidation, %	2.58	2.69	1.83	(~1.67)
C ₂ H ₄ Yield to EDC, %	94.8	93.8	94.3	92.5
HCl Yield to EDC, %	96.8	94.8	89.4	92.6
Productivity Lbs./EDC/ft. ³ /day** (Kg./EDC/28.3 Liters/day)	1098 (495)	698 (315)	1250 (560)	?

* The vent rate for the recycle process was based on an average molecular wt. of 37. The vent gas composition and the recycle gas composition are the same. For the existing process the vent gas had an average molecular weight of approximately 28.

** Productivity is defined as pounds of 1,2-dichloroethane produced per cubic ft. of catalyst volume per day.

¹ Penner U.S. Patent No. 3,184,515.

² Suzuki U.S. Patent No. 3,699,178.

Product Phase Analysis (Wt. %)	Present Process	Existing Process	Suzuki	Penner
C_2H_3Cl	0.038	0.3	—	0.0062
C_2H_5Cl	1.11	0.6	0.25	1.5278
CCl_4	0	0.148	—	—
Trans- $C_2H_2Cl_2$	0.052	0.108	—	0.02154
Cis- $C_2H_2Cl_2$	0.093	0.07	—	0.04639
C_2Cl_4	0	0.023	—	—
Sym- $C_2H_2Cl_4$	0.029	0.276	—	—
Unsym- $C_2H_2Cl_4$	0	0	—	—
Beta- $C_2H_3Cl_3$	0.59	0.5	2.4	0.6296
C_2HCl_5	0	0	—	—
C_2HOCl_3	0.19	0.232	—	0.80035
$C_2H_2Cl_2$ (EDC)	97.89	97.74	97.35	96.92
$CHCl_3$	Not found		—	0.01325
1,1- $C_2H_2Cl_2$	—	—	—	0.02816

Vent Gas	#Vent Gas/100 # EDC	Present Process	Existing Process	Suzuki*	Penner*
		1.7	63.7	71.1	96.6
Analysis Vent Gas	Mole Percent				
O ₂		1.93	2.13		2.69
N ₂		2.15	92.3		92.6
C ₂ H ₄		9.13	.64		.228
CO		39.3	1.15	—	.994
CO ₂		38.3	1.05	—	.921
CH ₄		6.07	.3	—	—
C ₂ H ₆		0.6	.1	—	—
C ₂ H ₄ Cl ₂ (EDC)		1.66	1.97	—	2.15
C ₂ H ₅ Cl		0.781	.3	—	.33
C ₂ H ₃ Cl		0.048	.03	—	.03

* Blank spaces indicate no data available in patent.

WHAT WE CLAIM IS:—

1. A process for preparing chlorinated hydrocarbons which comprises contacting a mixture of oxygen or a gas containing molecular oxygen, hydrogen chloride and an ethylenically unsaturated aliphatic hydrocarbon or a partially chlorinated ethylenically unsaturated aliphatic hydrocarbon, the oxygen being employed in a state of purity of not less than 50% with respect to noncondensable gases, in amounts of from 0.4 to 0.8 mole of oxygen and 1.8 to 2.2 moles of hydrogen chloride per mole of said unsaturated hydrocarbon, with a Deacon-type copper oxychlorination catalyst at a temperature and pressure at which oxychlorination occurs, treating the resulting oxychlorination reaction products with water to remove any unreacted hydrogen chloride, cooling the remainder of the products to remove the condensable chlorinated hydrocarbons and recycling sufficient remaining noncondensable gases to the reactor to supply from 30 to 60 percent of the feed.
2. A process as claimed in claim 1, in which the reaction is carried out in a plurality of tubular reactors which are externally cooled to maintain the temperature therein at from 180° to 350°C.
3. A process as claimed in claim 1 or claim 2 wherein said oxygen is employed in a state of purity of greater than 90% with respect to noncondensable gases.
4. A process as claimed in claim 1 or claim 2 wherein said oxygen is substantially pure oxygen.
5. A process as claimed in any one of the preceding claims wherein said oxygen is in admixture with steam.
6. A process as claimed in any one of claims 2 to 5 wherein each reactor is internally packed with an alumina carrier loaded with from 1 to 10% copper as copper chloride admixed with from 0 to 100% by weight inert diluent.
7. A process as claimed in claim 6 wherein the alumina carrier is loaded with from 2 to 7% copper as copper chloride.
8. A process as claimed in claim 6 wherein the alumina carrier is loaded with from 3 to 6.5% copper as copper chloride.
9. A process as claimed in any one of the preceding claims wherein the ethylenically unsaturated hydrocarbon is ethylene.
10. A process as claimed in any one of claims 2 to 9 wherein each tubular reactor contains a plurality of catalyst zones of increasing copper content from the inlet to the outlet of the reactor.
11. A process as claimed in any one of claims 2 to 10 wherein each tubular reactor has an internal diameter of from 0.5 inch to 3.0 inches and a length of from 10 to 60 feet.
12. A process as claimed in any one of claims 2 to 11 wherein each tubular reactor has an internal diameter of from 0.75 to 2.0 inches.
13. A process for preparing chlorinated hydrocarbons substantially as hereinbefore described in the Example.
14. A chlorinated hydrocarbon whenever prepared by a process as claimed in any one of the preceding claims.

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